

Polymer collapse in the presence of hydrodynamic interactions

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We investigate numerically the dynamical behaviour of a polymer chain collapsing in a dilute solution. The rate of collapse is measured with and without the presence of hydrodynamic interactions. We find that hydrodynamic interactions both accelerate polymer collapse and alter the folding pathway.

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I. INTRODUCTION

When a polymer is placed in solution hydrophobic interactions between monomers and solvent molecules can cause it to undergo a collapse transition to a compact state [1,2]. The statistical physics of the polymer transition from the extended to the collapsed state is well understood. However the dynamics of the transition and in particular the effect on that dynamics of the hydrodynamic properties of the solvent remains unclear. Therefore in this Letter we investigate numerically the dynamical behaviour of a polymer chain collapsing in a dilute solution. The collapse is measured with and without the presence of hydrodynamic interactions thus allowing a direct investigation of their effect. We find that hydrodynamics accelerates the polymer collapse. It also alters the folding pathway, allowing the folding to occur more homogeneously along the polymer chain rather than initially at the chain ends.

With the introduction of Zimm's model [2] it became apparent that hydrodynamics play a central role in the dynamics of polymers in dilute solution. However, understanding such interactions is difficult, analytically because they present a complicated many-body problem, and numerically because they develop on time-scales long compared to the thermal fluctuations of the monomers.

Theoretical work on the dynamics of polymer collapse can be divided into two approaches. Phenomenological models balance the driving and dissipative forces to give scaling laws [3–7]. They involve assumptions about how the collapsed state develops on which there is no consensus. Several authors have considered models which are based on a solution of the Langevin equation [8–10]. Of particular interest is work by Pitard [11] and by Kuznetsov et al [12] who find the inclusion of hydrodynamics, modelled by a preaveraged Oseen tensor, speeds up the collapse.

Simulations on polymer collapse [4,13–15], using Monte Carlo or Langevin approaches, have not included the hydrodynamic effects of the solvent. Very recent work has shown that it is now possible to use molecular dynamics simulations with an explicit solvent to model the collapse transition if powerful computational resources are available [7]. In an interesting recent paper Chang

and Yethiraj [16] compared molecular dynamics simulations of a polymer in a solvent to Brownian dynamics simulations. They attempted to match the parameters in the two simulations and hence to compare collapse with and without hydrodynamics. Here we use a hybrid approach [17] where the solvent is modelled by a Malevanets-Kapral method [18] and the polymer by molecular dynamics in our investigation of the hydrodynamics of polymer collapse.

II. SIMULATION DETAILS

Modelling a dilute polymer solution is a difficult task because of the existence of widely differing time scales. The dynamical properties of polymers can be dominated by hydrodynamic interactions between different parts of the polymer chains [2]. In contrast with the time scale of thermal fluctuations of individual monomers, these interactions are long-ranged and evolve slowly. Therefore it is computationally too expensive to reach hydrodynamic time scales using molecular dynamics simulations for both the polymer and the solvent molecules.

To overcome this problem we use a hybrid simulation approach where the equations of motion of the polymer alone are solved using a molecular dynamics algorithm. The solvent is modelled using a mesoscale approach, developed by Malevanets and Kapral [18]. This ignores the molecular detail of the solvent but preserves its ability to transmit hydrodynamic forces. The polymer can be thought of as moving within a “hydrodynamic heat bath”.

The polymer chain is modelled by beads connected via non-harmonic springs [19] with adjacent beads along the chain backbone representing an effective Kuhn length of the polymer chain. These finitely extensible springs are represented by the FENE potential

$$V_{FENE}(r) = -\frac{\kappa}{2}R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right], \quad r < R_0. \quad (1)$$

A Lennard-Jones potential [20] which acts between all the polymer beads is used to model the excluded volume of the monomers and a long range attraction which drives polymer collapse

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

We take $\varepsilon = 1.0$, $\sigma = 1.0$, $\kappa = 30$ and $R_0 = 2$ where parameters and results are quoted in reduced Lennard-Jones units.

Newton's equations of motion for the polymer are integrated using the time reversible velocity Verlet algorithm [20]. The molecular dynamics time step is chosen to be $\delta t = 0.002 t_s$ where t_s is the interval between solvent collision steps, defined below.

The solvent is modelled by a large number $N = 131072$ of point-like particles which move in continuous space with continuous velocities but discretely in time [18]. The algorithm is separated into two stages. In the first of these, a free streaming step, the positions of the solvent particles at time t , $\mathbf{x}_i(t)$, are updated simultaneously according to

$$\mathbf{x}_i(t+t_s) = \mathbf{x}_i(t) + \mathbf{v}_i(t)t_s \quad (3)$$

where $\mathbf{v}_i(t)$ is the velocity of a particle.

The second component of the algorithm is a collision step which is executed on both solvent particles and polymer beads. The system is coarse-grained into L^3 unit cells of a regular cubic lattice. In this simulation $L = 32$ is used. There is no restriction on the total number of solvent or polymer particles in each cell, although the total number of particles is conserved. Multiparticle collisions are performed within each individual cell of the coarse-grained system by rotating the velocity of each particle relative to the centre of mass velocity $\mathbf{v}_{cm}(t)$ of all the particles within that cell

$$\mathbf{v}_i(t+t_s) = \mathbf{v}_{cm}(t) + \mathbf{R}(\mathbf{v}_i(t) - \mathbf{v}_{cm}(t)). \quad (4)$$

\mathbf{R} is a rotation matrix which rotates velocities by θ around an axis generated randomly for each cell and at each time step. In the present calculations we take $\theta = \frac{\pi}{2}$.

Note that the collision step preserves the position of the solvent and polymer beads. It transfers momentum between the particles within a given cell while conserving the total momentum of these particles. Because both momentum and energy are conserved locally the thermohydrodynamic equations of motion are captured in the continuum limit [18]. Hence hydrodynamic interactions can be propagated by the solvent and, because the polymer beads are involved in the collisions, to the polymer. Note, however, that molecular details of the solvent are excluded: this allows the hydrodynamic interactions to be modelled with minimal computational expense.

The volume in phase space is invariant under both the free streaming and collision steps. Hence the system is described by a microcanonical distribution at equilibrium [18]. The initial solvent distribution was generated by assigning positions randomly within the system with an average density $\rho = 4$ particles per unit cell. The velocities were assigned from a uniform distribution which

relaxed rapidly ($t_s \leq 100$) to the equilibrium Maxwell-Boltzmann form.

A particularly useful feature of the Malevanets-Kapral algorithm is the ease with which hydrodynamic interactions can be “turned-off” thus replacing the hydrodynamic heat bath by a Brownian (random) heat bath. This is achieved by randomly interchanging the velocities of all the solvent particles after each collision step, thus relaxing the constraint of local momentum conservation to a global one. Accordingly the velocity correlations which result in hydrodynamic interactions disappear from the fluid. Running simulations with the same initial conditions and parameter values, but with hydrodynamics present or absent, greatly facilitates pinpointing the effect of the hydrodynamic interactions.

III. RESULTS

Our aim is to study the dynamics of polymer collapse from an extended to a compact state [1]. The collapse transition is driven by the attractive Lennard-Jones interactions between the polymer beads. The transition is rounded and shifted by the finite chain length, and takes place at $k_B T \sim 1.8$ for chains of length $N_p = 100$.

Initial polymer configurations were chosen at random from long runs on a polymer chain at equilibrium in a solvent with $k_B T = 4$. Each of these extended configurations were placed in a solvent at equilibrium at $k_B T = 0.8$. This value ensures collapse but prevents the chain collapsing so quickly that hydrodynamic interactions do not have sufficient time to develop. The rate of polymer collapse was measured by monitoring the variation of the radius of gyration R_g of the chain with time

$$R_g^2(t) = \frac{1}{N_p} \sum_{i=1}^{N_p} (R_i(t) - R_{cm}(t))^2, \quad (5)$$

$$R_{cm}(t) = \frac{1}{N_p} \sum_{i=1}^{N_p} R_i(t).$$

A typical numerical result is shown in Figure 1 for a chain of length $N_p = 100$ with and without hydrodynamics.

The collapse time was estimated as the time when the equilibrium radius of gyration was first attained. Results for τ are shown for chains of varying lengths in Table 1. τ was averaged over 20 initial configurations for $N_p = 40$, 60 and 100, and 5 for $N_p = 200$, and the collapse time for hydrodynamic (τ_H) and Brownian (τ_B) heat baths compared. Variations in collapse times between different runs are large as expected. However, it is strikingly apparent that hydrodynamic interactions speed up the rate of collapse by a factor ~ 2 for each polymer length. For all but 6 of the 65 runs and for all the $N_p = 100$ and 200 runs the collapse was faster with hydrodynamics

switched on. The results in Table 1 also illustrate that the collapse time increases with chain length as expected ($\tau_B \sim N_p^{1.6 \pm 0.2}$, $\tau_H \sim N_p^{1.2 \pm 0.3}$). Values predicted in the literature for the exponents relating the collapse time to chain length vary widely. It is far from obvious that these exponents are universal: they appear to depend on quench depth and the details of the model [16]. Moreover the final radius of gyration was recorded for both the Brownian and hydrodynamic collapses and found to agree as the equilibrium polymer properties should be independent of the nature of the heat bath.

Figure 2 compares typical collapse pathways with and without hydrodynamics for $N_p = 100$ and a final temperature $k_B T = 0.8$. In this and the majority of other runs a qualitative difference was observed in the collapse mechanism. In the Brownian solvent the ends of the polymer tend to collapse first forming a dumbbell shape. With hydrodynamics the collapse takes place more evenly along the chain. We speculate that this occurs due to 'slipstreaming'. The movement of beads towards each other, which is initiated by the attractive Lennard-Jones potential, is enhanced by hydrodynamic interactions. Once a bead starts moving in a given direction and locally drags fluid with it, it is easier for neighbouring beads to move in the same direction. Similar behaviour albeit on much larger length scales has been observed experimentally by Bartlett et al [21] for a pair of colloidal particles in solution.

IV. DISCUSSION

We have shown that it is possible to measure the dynamics of the collapse transition of a polymer in a solvent using a hybrid mesoscale/molecular dynamics algorithm. Hence it has been possible to show that hydrodynamic interactions speed up the collapse of the polymer chain. The hydrodynamics alters the collapse pathway, allowing the folding to occur more homogeneously along the chain, rather than initially at the chain ends.

Qualitative features of the collapse pathways are in agreement with those reported by Chang and Yethiraj [16] who recently compared molecular dynamics simulations of a polymer in a solvent, which include hydrodynamics, to Brownian dynamics simulations, which did not. These authors also found that the Brownian simulations could become trapped in a metastable free energy minimum. It would be interesting to address whether this is due to deeper quenches than those considered here or to the different simulation approaches employed.

The solvent is modelled using the Malevanets-Kapral algorithm which sustains hydrodynamic modes but does not include molecular interactions. Hence we caution that we cannot investigate the late stages of collapse where trapping of the water molecules in the polymer

chain may be important. Moreover collapse is driven by attractive Lennard-Jones interactions between the polymer beads rather than repulsive monomer-solvent interactions. It would be of interest to include the solvent near the polymer in the more realistic molecular dynamics updating and the possibility of doing this is under investigation.

Finally it may be of interest to consider whether the early stages of the folding of proteins in aqueous solution might be influenced by the hydrodynamic interactions of the solvent increasing the cooperativity of the collapse.

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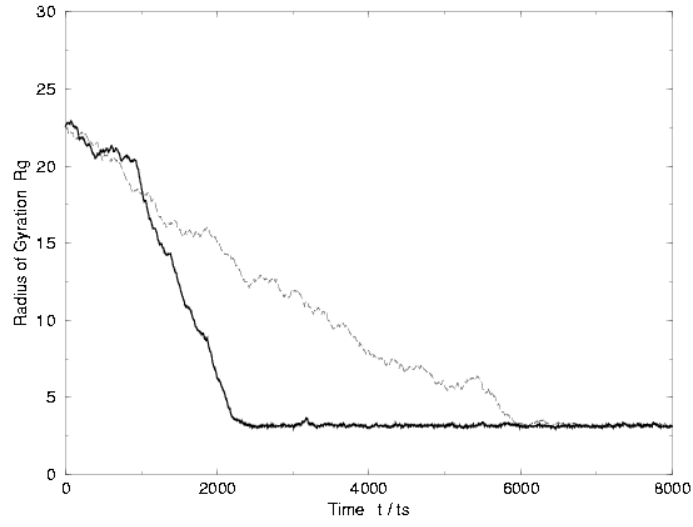


FIG. 1. Variation of the radius of gyration with time for a collapsing polymer chain in a hydrodynamic (—) or Brownian (···) heat bath.

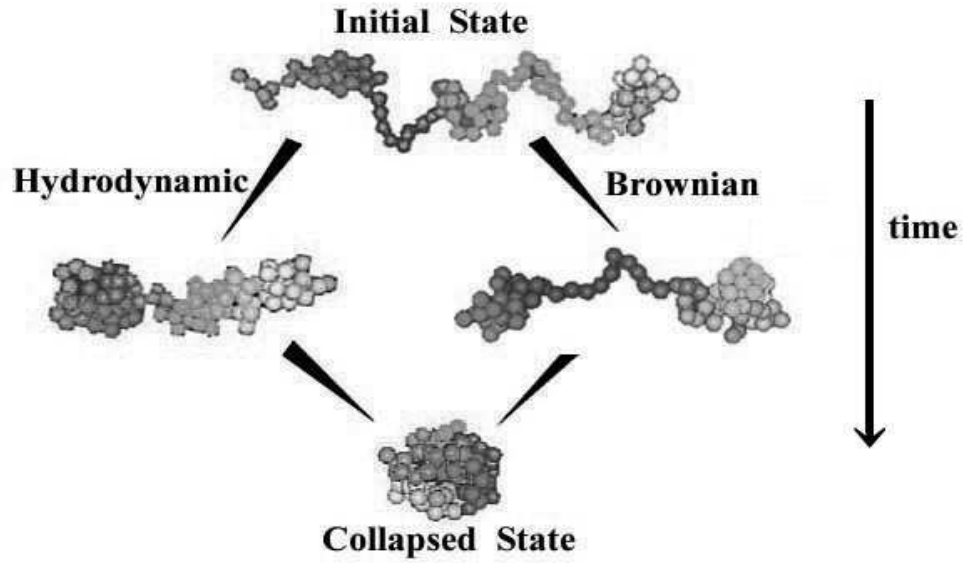


FIG. 2. A comparison of the pathways for polymer collapse with and without hydrodynamics.

N_p	$\langle\tau_H\rangle$	$\langle\tau_B\rangle$	$\langle R_{g_H}\rangle$	$\langle R_{g_B}\rangle$
40	290 ± 92	401 ± 118	2.02 ± 0.05	2.02 ± 0.04
60	490 ± 79	671 ± 170	2.23 ± 0.02	2.23 ± 0.01
100	858 ± 113	1571 ± 252	2.58 ± 0.01	2.58 ± 0.02
200	2050 ± 253	5500 ± 390	3.15 ± 0.00	3.16 ± 0.02

TABLE I. Averaged collapse time in units of the solvent time step t_s of a polymer chain of length N_p with ($\langle\tau_H\rangle$) and without ($\langle\tau_B\rangle$) hydrodynamics for a final temperature $k_B T = 0.8$. The radius of gyration after collapse in reduced Lennard-Jones units with ($\langle R_{g_H}\rangle$) and without ($\langle R_{g_B}\rangle$) hydrodynamics is also listed.